

IN THE SPECIFICATION:

Please amend paragraph number [0004] as follows:

[0004] The performance of CL-20 in propellant and weapon systems is highly dependent upon the crystal polymorph of CL-20. CL-20 may undertake several different crystal polymorphs, the most preferred of which is a high density phase known in the art and referred to herein as the ϵ -polymorph (or epsilon-polymorph) of CL-20. The ϵ -polymorph of CL-20 is preferred because of the high energetic performance and density, and lower sensitivity compared to other polymorphs. However, many conventional CL-20 synthesis techniques produce non-epsilon polymorphs, especially α -polymorph, in relatively large amounts. The α -polymorph has a much lower density ~~that than~~ the ϵ -polymorph, and, therefore, is less desirable for use in propellant weapon systems. For these reasons, CL-20 synthesized by many conventional techniques must be dissolved and subjected to re-crystallization in order to increase the yield of the ϵ -polymorph to acceptable levels.

Please amend paragraph number [0006] as follows:

[0006] The technique of the Johnston et al. patent is particularly effective over most conventional methods in crystallizing ϵ -polymorph CL-20 prepared from its TADF (tetraacetyldiformylhexaazaisowurtzitane) precursor. However, application of the same crystallization technique to CL-20 prepared from its TADA (2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{5,9}.0^{3,11}]-dodecane or "TADH") precursor has certain drawbacks. In particular, addition of the non-solvent to the dry CL-20 solvent solution causes precipitating CL-20 crystals to stick to the crystallizer —~~e.g., container, beaker, or tank~~—(e.g., container, beaker, or tank) in which the crystallization is conducted. In some instances, as much as 10 to 20 weight percent of the CL-20 crystal yield remains stuck to the crystallizer walls. In order to remove the precipitated CL-20 crystals from the crystallizer, the CL-20 crystals are redissolved into solution with a CL-20 solvent, such as ethyl acetate, then are recrystallized with a non-solvent. With each recrystallization, a smaller amount of precipitate sticks to the crystallizer walls. Often, however, this process must be repeated several times to produce a high yield

without leaving appreciable amounts of CL-20 stuck to the crystallizer. In addition, the crystals form as unusable large agglomerates because of the inability to grow on all surfaces of the crystal.

Please amend paragraph number [0009] as follows:

~~Objects of the Invention~~SUMMARY OF THE INVENTION

[0009] ~~It is, therefore, an object of this invention to overcome a need in the art by providing~~The present invention relates to a method that produces of producing ϵ -polymorph (epsilon polymorph) CL-20 crystals, especially but not necessarily CL-20 crystals made from the TADA precursor, without encountering significant amounts of sticking of crystallized CL-20 to the walls of the crystallizer.

Please amend paragraph number [0010] as follows:

[0010] ~~It is another object of this invention to provide~~The present invention also relates to a method that produces ϵ -polymorph (epsilon polymorph) CL-20 particles, especially but not necessarily CL-20 particles made from the TADA precursor, of desirable size distribution without requiring post-crystallization grinding operations.

Please delete paragraph number [0011] as follows:

[0011] ~~Additional objects and advantages of the invention will be set forth in the description that follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations pointed out in the appended claims.~~

Please amend paragraph number [0012] as follows:

~~SUMMARY OF THE INVENTION~~

[0012] In accordance with the principles of this invention, ~~the above and other objects may be attained by a first aspect of this invention in which~~ 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0^{5,9}.0^{3,11}]-dodecane (CL-20 or HNIW) is crystallized to its ϵ -polymorph by a novel method. According to ~~this~~ a first aspect, the crystallization method comprises preparing a substantially dry CL-20 solvent solution containing an amount of CL-20 dissolved in a CL-20 solvent. The substantially dry solvent solution is added to a crystallizer containing a CL-20 non-solvent to cause precipitation of epsilon polymorph CL-20 crystals by an inverse precipitate technique. The precipitated epsilon polymorph CL-20 crystals are separated from the non-solvent and the solvent.

Please amend paragraph number [0015] as follows:

[0015] In accordance with ~~a preferred~~ an embodiment of each of the above aspects of the invention, the sequence of adding the substantially dry CL-20 solvent solution to the non-solvent ~~—also known as inverse precipitation—~~ (also known as inverse precipitation) substantially reduces or eliminates the sticking of precipitated epsilon-polymorph CL-20 crystals to the wall or walls of the crystallizer in which the inverse precipitation technique is carried out. Also within ~~a preferred~~ an embodiment of each of the above aspects of the invention, the resulting CL-20 particles have a relatively narrow particle size distribution. For example but not necessarily by limitation, the precipitated epsilon polymorph CL-20 crystals may comprise particles having maximum diameters of, on average, about 40 μm to about 70 μm .

Please amend paragraph number [0016] as follows:

[0016] In accordance with another ~~preferred~~ embodiment of each of the above aspects of the invention, the wet CL-20 solvent solution is substantially dried by a process comprising azeotropic distillation to remove an azeotrope comprising water and the CL-20 solvent.

Preferably, the dry CL-20 solvent solution is substantially dry and contains less than 1.5 weight percent water.

Please amend paragraph number [0018] as follows:

[0018] It is also within the scope of this invention to add a co-non-solvent to the wet CL-20 solvent solution or the dry solvent solution. In one ~~preferred~~ variation of the invention, the co-non-solvent comprises at least one member selected from the group consisting of naphthenic oil, paraffinic oil, and poly(propylene glycol). The weight ratio of co-non-solvent to non-solvent may be, for example, in a range of from about 5:95 to about 20:80.

Please amend paragraph number [0020] as follows:

[0020] In accordance with another ~~preferred, but not necessarily limiting~~, embodiment of each of the above aspects of the invention, the method further comprises preparing the CL-20 from 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazatetracyclo-[5.5.0.0^{5,9}0^{3,11}]-dodecane (TADA).

Please delete paragraph number [0022] as follows:

~~[0022] Other objects, aspects, and advantages of this invention will become more apparent to those skilled in the art upon reading the specification and appended claims, which explain the principles of this invention.~~

Please amend paragraph number [0027] as follows:

[0027] With the CL-20 dissolved in a solvent, a base (in either solid or solution form) may optionally be added to ensure removal of all acidic species. The pH of the aqueous layer can be tested and adjusted to a pH greater than 7 with Na₂CO₃ or a similar base (NaHCO₃, K₂CO₃, KHCO₃ NaOH, KOH, etc.). It has been reported that the presence of acidic species in the crystallized CL-20 increases the sensitivity to impact and friction. The base can be added to the system at any point where the CL-20 is dissolved in the solvent. ~~In some cases it is desirable add~~

~~the base as final step prior to CL-20 crystallization.~~In some cases, it is desirable to add the base as a final step prior to CL-20 crystallization.

Please amend paragraph number [0029] as follows:

[0029] It is preferable to azeotrope under conditions ~~which that~~ remove the CL-20 solvent/water azeotrope without reducing the solvent to a level below that needed to keep the CL-20 soluble. Removal of too much of the CL-20 solvent may cause the CL-20 to crystallize prematurely. The solution is dried, preferably at low temperature under vacuum. Those skilled in the art will appreciate that a wide range of operating temperatures and pressures are possible to achieve the desired water removal.

Please amend paragraph number [0030] as follows:

[0030] The dry CL-20 solution is fed into a crystallizer ~~—such as a container—~~(such as a container) containing CL-20 non-solvent and optionally other materials, such as seed crystals of CL-20. Non-solvents that are suitable for use in the present invention preferably have boiling points that will allow for separation from the solvent by distillation. Although not necessarily by limitation, the non-solvents preferably have poor CL-20 solubility of not more than 5% weight/volume (g/ml), more preferably not more than 1% weight/volume (g/ml), of CL-20 in the non-solvent. Representative non-solvents include the following: ~~alkanes-alkanes~~, such as heptane, hexane, and octane; alicyclic alkanes, such as cycloheptane; arenes, such as benzene, toluene, and xylene; and halogenated hydrocarbons, such as chloroform, 1,2-dichloroethane, and bromobenzene. Certain formates and acetates may also be used. Examples of aryl formates include, by way of example only, phenyl formate, phenalkyl formates, such as benzyl formate and phenethylformate; and benzoyl formates, such as 1-methylpropyl benzoyl formate. The aryl formate can also contain substituents, such as in the case of 4-methoxy benzyl formate, multiple formate moieties, and/or heteroatoms. Non-aromatic formates, such as alkylformate (e.g., heptylformate), ethylene glycol diformate, triethylene glycol diformate, and diethylene glycol diformate, can also be selected as the non-solvent. Examples of aryl acetates include, by way of

example, phenyl acetate; phenalkyl acetates, such as benzyl acetate and phenethyl acetate; and benzoyl acetates, such as 1-methylpropyl benzoyl acetate. The aryl acetate can also contain substituents, such as in the case of 4-methoxy benzyl acetate, multiple acetate moieties, and/or heteroatoms. Non-aromatic acetates, such as alkylacetates (e.g., heptyl acetate), ethylene glycol diacetate, triethylene glycol diacetate, and diethylene glycol diacetate, can also be selected as the non-solvent. However, if one of these non-solvents is selected, then the CL-20 solvent will preferably have a different boiling point from the non-solvent to permit separation and recovery of the CL-20 solvent and the non-solvent.

Please amend paragraph number [0032] as follows:

[0032] It is particularly preferred that the non-solvent be used in combination with co-non-solvents, and in particular naphthenic and/or paraffinic oils. Preferred co-non-solvents include STAN-PLAS 100, STAN-PLAS 300, STAN-PLAS 500, ~~STANPLAS 1200~~ STAN-PLAS 1200, SUNPAR 120, and SUNPAR 150, which are examples of refined naphthenic oils and paraffinic oils. ~~Stan-Plas~~ Stan-Plas® oils are distributed through Harwick Standard Distribution Corporation. Other useful co-non-solvents are benzyl formate and/or poly(propylene glycol) (PPG). Other co-non-solvents include hydrocarbons, such as hexane, heptane, octane, and higher chain lengths, as well as branched, cyclic, aromatic (e.g., xylene and toluene), and halogenated hydrocarbons. Ethers, especially those having acceptable boiling points for separation from the solvents in post-crystallization operations, can also be used as the co-non-solvent. Preferred co-non-solvents improve the polymorph and crystal geometry of the resulting CL-20 particles. Preferably, the co-non-solvent is present in a weight ratio of co-non-solvent to non-solvent of from about 5:95 to about 20:80. The co-non-solvent amount is preferably determined by the concentration that will produce the highest yield while maintaining acceptable monocrystalline geometry. It is within the scope of the invention to use the co-non-solvent as the exclusive non-solvent.

Please amend paragraph number [0049] as follows:

[0049] 50 grams of dry CL-20 (derived from TADA) were dissolved in 110.0 grams of ethyl acetate to provide a CL-20 solvent solution. 12.0 grams of ~~Stan-Plas~~[®]-Stan-Plas[®] were added. The solution was then added to 1000 ml of heptane non-solvent at a rate of about 30 ml per minute while stirring. The CL-20 crystallized via inverse precipitation technique, and a yield of 48.51 grams of CL-20 was recovered. Little or no CL-20 crystals adhered to the crystallizer.

Please amend paragraph number [0050] as follows:

[0050] 50 grams of dry CL-20 (derived from TADA) were dissolved in 110.0 grams of ethyl acetate to provide a CL-20 solvent solution. 6.0 grams of ~~Stan-Plas~~[®]-Stan-Plas[®] and 6.0 grams of benzyl formate were added, and the solution was mixed until homogeneous. The solution was then added to 500 ml of heptane non-solvent having seed crystals at a rate of about 30 ml per minute while stirring. The precipitated crystals were filtered to provide a recovery of 39.41 grams. Little or no CL-20 crystals adhered to the crystallizer.

Please amend paragraph number [0052] as follows:

[0052] The procedure of Comparative Example A was repeated on a CL-20 solvent solution containing 50 grams of TADA CL-20 dissolved in 100 grams of ethyl acetate. Ethanol was selected as the ~~non-solvent~~, non-solvent and was added at a rate of approximately 1 to 1.5 ml per minute until 400 ml of ethanol were added. 22.46 grams of CL-20 were formed, but a substantial amount adhered to the glass.